



UNIVERSITI PUTRA MALAYSIA

**PREPARATION AND PHYSICO-CHEMICAL CHARACTERISATION
OF VPO AND V₂O₅/TiO₂ CATALYSTS**

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By

GOH CHEE KEONG

**Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirements for the degree of Master of Science

**PREPARATION AND PHYSICO-CHEMICAL CHARACTERISATION OF
VPO AND V_2O_5/TiO_2 CATALYSTS**

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July 2002

Chairman: Associate Professor Taufiq Yap Yun Hin, Ph.D, C'Chem, MRSC

Faculty: Science and Environmental Studies

Vanadium-based catalyst plays an important role in petrochemical industry. In this study, two types of vanadium-based catalysts were synthesised. They are vanadium phosphorus oxide and vanadia-titania catalysts. Vanadium phosphorus oxide catalysts were synthesised via two different precursors, as $VOHPO_4 \cdot 0.5H_2O$ and $VO(H_2PO_4)_2$. Vanadium phosphorus oxide catalysts obtained from $VOHPO_4 \cdot 0.5H_2O$ precursor were prepared by "organic medium" (denoted as VPO_O route) and the reduction of $VOPO_4 \cdot 2H_2O$ (denoted as VPO_I route). These catalysts were modified by three metal ions, Ba^{2+} , Fe^{3+} and Mn^{2+} . The vanadium phosphorus oxide catalysts derived from $VO(H_2PO_4)_2$ precursor were prepared by two methods: i) reaction between V_2O_4 with phosphoric acid and ii) reduction of $VOPO_4 \cdot 2H_2O$ by using 3-octanol. On the other hand, the vanadia-titania catalysts were prepared via impregnation and solid state methods. The catalysts derived from $VO(H_2PO_4)_2$ displayed the excess of phosphorus in bulk and surface composition analysis. The promoted vanadium phosphorus oxide catalysts which were prepared in VPO_O and VPO_I route gave the P/V ratios in a range

0 98-1 13 for bulk and surface composition analysis Surface area is a one of the major factors controlling catalyst activity Hence, the difference in preparation procedures of vanadium-based catalysts would lead to the difference values of the surface area The main characteristic reflection of $(VO)_2P_2O_7$ phase was present for the unpromoted and promoted catalysts prepared by both $VPO_{(1)}$ and $VPO_{(1)}$ route In addition, the V^{5+} phase was detected for ferrite and manganese promoted catalysts which prepared by $VPO_{(1)}$ route The XRD results of the catalysts derived from $VO(H_2PO_4)_2$ gave partly crystalline $VO(PO_3)_2$ There were no V_2O_5 phases detected in the XRD results of the vanadia-titania catalysts because of the low concentration of V_2O_5 The presence of the plane linkage bonding of $V=O$, $V-O-V$ and $P-O-P$ in the FTIR spectra of the vanadium phosphorus oxide catalysts indicated that the phosphorus and vanadium linkage of two (100) plane of the catalysts The shifting in the FT-IR absorption bands of the $V=O$ stretching mode for promoted vanadium phosphorus oxide catalysts showed that the promoter elements would incorporate into the crystal lattice of $(VO)_2P_2O_7$ The interactions of the $V=O$ vibration of the vanadia-titania catalysts were studied by the FTIR technique The SEM micrographs showed the principal morphologies of the vanadium phosphorus oxide catalysts were consisted of the plate-like crystals The vanadia-titania catalysts displayed the granular-like crystallites with the size approximately $1\ \mu m$ The TPD results indicated the $VPDFe1.0$ catalyst has higher total amount of oxygen desorbed from the surface of the catalysts It was clear that the results from TPR gave the values of the total amount of oxygen removed from the surface of the catalysts much higher than the values of the total amount of oxygen desorbed

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN DAN PENCIRIAN MANGKIN VPO DAN V_2O_5/TiO_2

Oleh

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Mangkin vanadium memainkan peranan yang penting dalam industri petrokimia. Dalam kajian mangkin vanadium fosforus oksida dan vanadia-titania, mangkin vanadium fosforus oksida telah disintesis melalui dua prekursor yang berlainan, iaitu $VOHPO_4 \cdot 0.5H_2O$ dan $VO(H_2PO_4)_2$. Mangkin vanadium fosforus oksida yang diperolehi daripada $VOHPO_4 \cdot 0.5H_2O$ prekursor boleh disediakan daripada "medium organik" (ditandakan sebagai kaedah VPO_(i)) dan proses penurunan $VOPO_4 \cdot 2H_2O$ (ditandakan sebagai kaedah VPO_(ii)). Mangkin ini telah diubahsuai dengan tiga jenis ion logam, iaitu Ba^{2+} , Fe^{3+} dan Mn^{2+} . Sementara mangkin vanadium fosforus oksida yang diperolehi daripada $VO(H_2PO_4)_2$ prekursor telah disediakan dengan dua kaedah: i) tindak balas antara V_2O_5 dengan asid fosforik dan ii) proses penurunan $VOPO_4 \cdot 2H_2O$ oleh 3-oktanol. Di samping itu, mangkin vanadia-titania telah disediakan melalui kaedah impregnasi dan mekanikal. Mangkin yang diperolehi daripada $VO(H_2PO_4)_2$ menunjukkan komposisi fosforus yang berlebihan dalam pukal dan permukaan komposisi analisis. Mangkin vanadium fosforus oksida yang telah diubahsuai memberikan nisbah P/V dalam julat 0.98-1.13 untuk pukal.

dan permukaan komposisi analisis. Luas permukaan merupakan salah satu faktor yang penting dalam pengawalan aktiviti mangkin. Fasa $(VO)_2P_2O_7$ merupakan sifat utama yang muncul dalam mangkin yang disediakan melalui kedua-dua kaedah VPO_6 dan VPO_1 . Selain daripada itu, fasa V^{5+} juga dikesan bagi mangkin yang diubahsuai dengan logam ferum dan mangan yang disediakan melalui kaedah VPO_6 . Keputusan XRD untuk mangkin yang diperolehi daripada $VO(H_2PO_4)_2$ telah menghasilkan $VO(PO_3)_2$ yang separa kristal. Tiada sebarang fasa V_2O_5 yang dapat dikesan dalam XRD untuk mangkin vanadia-titania kerana kuantiti V_2O_5 yang terlalu sedikit. Kehadiran permukaan ikatan $V=O$, $V-O-V$ dan $P-O-P$ dalam spektra FTIR untuk mangkin vanadium fosforus oksida menunjukkan bahawa terdapatnya hubungan antara fosforus dan vanadium dalam permukaan (100) bagi mangkin tersebut. Perubahan penyerapan FTIR dalam getaran $V=O$ untuk mangkin vanadium fosforus oksida yang telah diubahsuai menunjukkan bahawa unsur-unsur tersebut telah memasuki dalam fasa $(VO)_2P_2O_7$. Hubungan antara getaran $V=O$ untuk mangkin vanadia-titania telah dikaji dengan teknik FTIR. Mikrograf SEM telah menunjukkan morfologi yang utama untuk mangkin vanadium fosforus oksida adalah mengandungi struktur yang menyerupai kepingan. Mangkin vanadia-titania menunjukkan struktur yang menyerupai butiran dengan saiznya lebih kurang $1\ \mu m$. Keputusan TPD menunjukkan $VPDFe1.0$ mengandungi jumlah oksigen yang dijerap dari permukaan mangkin yang tinggi. Ini adalah jelas bahawa TPR memberikan nilai jumlah oksigen yang dilepaskan dari permukaan mangkin adalah sangat tinggi daripada nilai jumlah oksigen yang dijerap.

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I certify that an Examination Committee met on 8th July, 2002 to conduct the final examination of Goh Chee Keong on his Master of Science thesis entitled "Preparation and Physico-chemical Characterisation of VPO and V₂O₅/TiO₂ Catalysts" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulation 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows

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DECLARATION FORM

I hereby declare that the thesis is based on my original work except for quotations and citations which have been acknowledged. I also declare that it has not been previously or currently submitted for any other degree at UPM or other institutions.



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LIST OF ABBREVIATIONS

ASAP	Analysis of surface area and porosity
B.E.T.	Brunauer-Emmet-Teller
CHN	Carbon hydrogen nitrogen
CMAS	Crystallographic model of active sites
E_d	Desorption activation energy
E_r	Reduction activation energy
EDX	Energy dispersive X-ray
ESR	Electron spin resonance
FHWM	Full width at half maximum
FTIR	Fourier transform infrared
GHSV	Gas hour space velocity
h	Hours
ICP-AES	Inductively coupled plasma atomic emission spectrometer
JCPDS	Joint Committee on Powder Diffraction Standards
JEOL	Japan Electron Optics Laboratory
LRS	Laser Raman spectroscopy
MA	Maleic anhydride
MAS	Magic angle spinning
NMR	Nucleus magnetic resonance
PA	Phthalic anhydride
PVC	Polyvinyl chloride
RED	Radial electron distribution



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SEM	Scanning electron microscopy
TCD	Thermal conductivity detector
TG	Thermogravimetric
TPD	Temperature-programmed desorption
TPR	Temperature-programmed reduction
TRXAS	Time-resolved <i>in situ</i> X-ray absorption spectroscopy
UPE	Unsaturated polyester
VPO	Vanadium phosphorus oxide
VPO _O	Organic method
VPO _D	Dihydrate method
XPS	X-ray photoelectron
XRD	X-ray diffraction

CHAPTER 1

INTRODUCTION

1.1 General

Catalysis plays an important role in our life, environmental and economy. About 80 % of all chemicals that are produced have been in contact with one or more catalysts somewhere in their synthesis process [1]. Besides, catalysis can be used to solve the environmental pollution problems, such as the three-way catalyst effectively reduces the level of CO_x , NO_x and VOC's in automotive exhaust gases [2]. The other function for catalyst is in improving the existing process to achieve a higher product yield that has economical values.

Initially, the term "catalysis" comes from two Greek words, "catal" and "lysein" which means breaking down. It was firstly introduced by J.J. Berzelius in 1836. He defined the catalysis as "the ability of substances to awaken affinities, which are asleep at a particular temperature, by their mere presence and not by their own affinity" [3]. Later, in 1895, William Ostwald wrote the definition of catalysis as "substances which change the velocity of a reaction without modification of the energy factors of the reaction" [4]. Nowadays, a catalyst can be defined as the substance that increases the rate at which a chemical system approaches equilibrium, without being consumed in the process.

Catalysis occurs when there is a chemical interaction between catalyst and the reactant-product system without changing the chemical nature of the catalyst except at the surface. This means that there is a surface interaction and does not penetrate into the interior of the catalyst [3].

1.2 Classification of Catalytic System

Catalytic system can be divided into two major categories,

- i) heterogeneous
- ii) homogeneous

A heterogeneous catalysis is a system where the catalyst and reactant are in a different phase. Hence, there is a phase boundary separates the catalyst from the reactant [3]. A number of phase combinations is occurred, for example solid-liquid phase in decomposition of hydrogen peroxide catalysed by gold, solid-gas phase in ammonia synthesis catalysed by iron, liquid-gas phase in polymerization of alkenes catalysed by phosphoric acid. Heterogeneous catalysis normally depends on at least one reactant being adsorbed (usually chemisorbed) and modified to a form in which it readily undergoes reaction [5].

When the catalyst is of the same phase as the reactant and no phase boundary exists, it can be defined as homogeneous catalysis [3]. This may happen either in the gas phase, for example, the nitrogen oxide catalyses the oxidation of sulphur dioxide [3].

1.3 Catalytic Oxidation

1.3.1 Selective Oxidation Reactions

Oxidation reactions play important role in modern chemical industry because more than 60 % of products obtained by catalytic route are products of oxidation [6] The reason is that oxygen (pure or in air) is cheap and possesses the high reactivity necessary to activate saturated hydrocarbons to valuable and economical products [7] Vinyl chloride, acrylates, methacrylates, ethylene oxide, acetic acid and maleic anhydrides which produced from saturated or non-saturated C_2-C_8 hydrocarbons are obtained by heterogeneous selective oxidation on metal oxide catalysts [8] The oxidation reactions studied in the last 30 years and main components of catalysts used in these reactions are listed in Table 1.1

Oxidation processes are defined as conversions of compounds under the influence of various oxidizing agents in organic chemistry. A distinction is made between complete and partial oxidation. Complete oxidation is an undesirable side process in organic synthesis which leads to the formation of CO , CO_2 and H_2O . It is partial oxidation which is important because it produces valuable intermediate products [7]

Table 1.1 Selective oxidation reactions of hydrocarbons and catalysts [9]

Reactions		Catalysts (main components)
A) With preservation of number of C atoms		
1. Olefins	→ unsaturated aldehydes	
	→ unsaturated acids	
	→ nitrile	
	→ dienes (ODH) ^a	
	→ organic oxides	
e.g. <u>propene</u>	→ <u>acrolein</u>	<u>BiMoPO</u>
	<u>acrylic acid</u>	<u>CoMoTeO, BiMoPO + VMoO</u>
	<u>acrylonitrile</u>	<u>MCM^b [BiFeCo(NiMg)MoO</u>
		<u>VSbO, FeSbO</u>
butene	→ butadiene	BiMoO
<u>ethene</u>	→ <u>ethene oxide</u>	<u>Ag(O)</u>
2. Alkanes	→ olefins (ODH)	
	→ aldehydes	
	→ acids	
e.g. propane	→ propene	VMgO, Ni(Co)MoO
propane	→ acrolein, acrylic acid	MoVNbSbO
<u>n-butane</u>	→ <u>maleic anhydride</u>	<u>VPO</u>
isobutane	→ methacrylic acid	HPC ^c [Cs(PMoVO)]
3. Alkylaromatics	→ aldehydes	
	→ anhydrides, acids	
e.g. toluene	→ benzaldehyde, benzoic acid	VTiO
<u>o-xylene</u>	→ <u>phthalic anhydride</u>	<u>VTiO</u>
B) With partial degradation of a molecule		
1. Olefins	→ saturated aldehydes and acids	
e.g. propene	→ acetaldehyde, acetic acid	V ₂ O ₅
2. aromatics		
e.g. <u>benzene</u>	→ <u>maleic anhydride</u>	<u>VMoO</u>
<u>naphthalene</u>	→ <u>phthalic anhydride</u>	<u>VKO</u>

^aODH oxidative dehydrogenation^bMCM multicomponent molybdates^cHPC heteropolycompounds (polyoxometalates)

Those applied on the industrial scale are underlined.